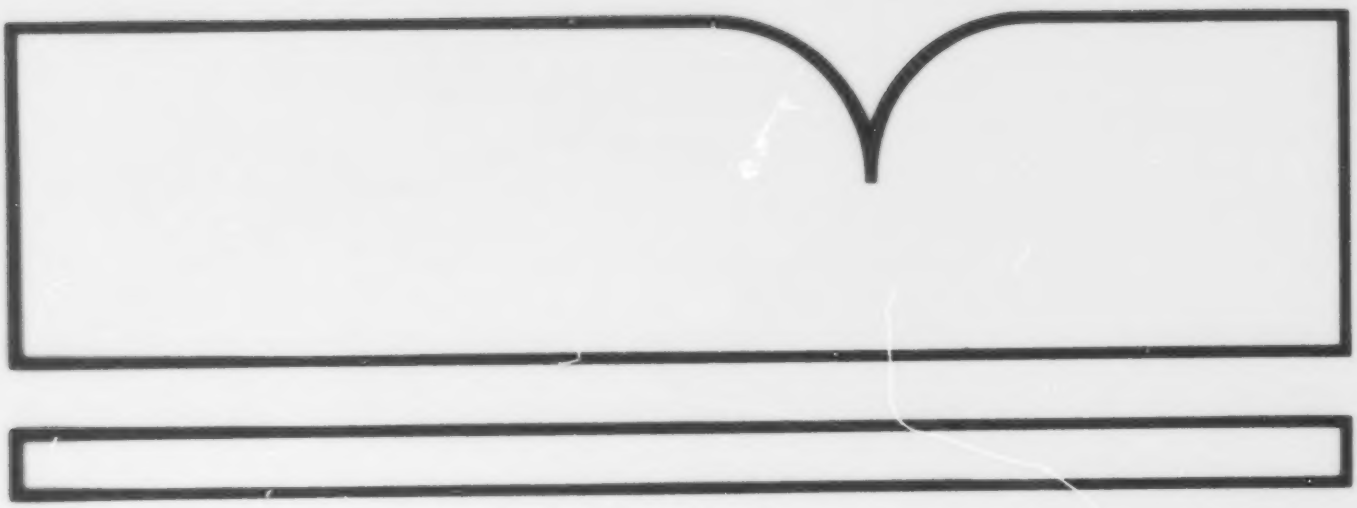
PB88-174578

Health and Environmental Effects Profile for Benzal Chloride

(U.S.) Environmental Protection Agency
Cincinnati, OH

Jan 85



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National Technical Information Service
NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/X-85/046	2.	3. RECIPIENT'S ACCESSION NO. PB88-174578
4. TITLE AND SUBTITLE Health and Environmental Effects Profile for Benzal Chloride		5. REPORT DATE January 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Criteria and Assessment Office Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/22
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

The Health and Environmental Effects Profile for benzal chloride was prepared by the Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Cincinnati, OH for the Office of Solid Waste and Emergency Response to support listings of hazardous constituents of a wide range of waste streams under Section 3001 of the Resource Conservation and Recovery Act (RCRA) and to provide health-related limits for emergency actions under Section 101 of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Both published literature and information obtained from Agency program office files were evaluated as they pertained to potential human health, aquatic life and environmental effects of hazardous waste constituents.

Quantitative estimates have been presented provided sufficient data are available. Existing data are insufficient to determine an Acceptable Daily Intake (ADI) or a carcinogenic potency factor for benzal chloride.

The Reportable Quantity (RQ) value of 1, 10, 100, 1000 or 5000 pounds is used to determine the quantity of a hazardous substance for which notification is required in the event of a relase as specified by CERCLA based on chronic toxicity. Existing data are insufficient to determine an RQ value.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field Group
18. DISTRIBUTION STATEMENT Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 25 22. PRICE A03 12.95

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB88-174578

EPA/600/X-85/046
January 1985

HEALTH AND ENVIRONMENTAL EFFECTS PROFILE FOR BENZAL CHLORIDE

ENVIRONMENTAL CRITERIA AND ASSESSMENT OFFICE
OFFICE OF HEALTH AND ENVIRONMENTAL ASSESSMENT
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

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PREFACE

Health and Environmental Effects Profiles (HEEPs) are prepared for the Office of Solid Waste and Emergency Response by the Office of Health and Environmental Assessment. The HEEPs are intended to support listings of hazardous constituents of a wide range of waste streams under Section 3001 of the Resource Conservation and Recovery Act (RCRA). Both published literature and information obtained from Agency program office files are evaluated as they pertain to potential human health, aquatic life and environmental effects of hazardous waste constituents. The literature searched and the dates of the searches are included in the section titled "Appendix: Literature Searched." The literature search material is current through November, 1984.

Quantitative estimates are presented provided sufficient data are available. For systemic toxicants, these include Acceptable Daily Intakes (ADIs) for chronic exposures. An ADI is defined as the amount of a chemical to which humans can be exposed on a daily basis over an extended period of time (usually a lifetime) without suffering a deleterious effect. In the case of suspected carcinogens, ADIs are not estimated in this document series. Instead, a carcinogenic potency factor of q_1^* (U.S. EPA, 1980) is provided. These potency estimates are derived for both oral and inhalation exposures where possible. In addition, unit risk estimates for air and drinking water are presented based on inhalation and oral data, respectively.

The first draft of this document was prepared by Syracuse Research Corporation under EPA Contract No. 68-03-3228. The document was subsequently revised after reviews by staff within the Office of Health and Environmental Assessment: Carcinogen Assessment Group, Reproductive Effects Assessment Group, Exposure Assessment Group, and the Environmental Criteria and Assessment Office in Cincinnati.

The HEEPs will become part of the EPA RCRA and CERCLA dockets.

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LIST OF ABBREVIATIONS

ADI	Acceptable daily intake
bw	Body weight
CNS	Central nervous system
LC_{50}	Concentration lethal to 50% of recipients
LD_{50}	Dose lethal to 50% of recipients
ppm	Parts per million

1. INTRODUCTION

1.1. STRUCTURE AND CAS NUMBER

The Chemical Abstracts name for this compound is benzene(dichloromethyl)-. Other synonyms are benzyl dichloride, benzylene chloride, benzylidine chloride, chlorobenzal, dichlorophenylmethane and α, α-dichlorotoluene (IARC, 1982). The structural and empirical formulae, and the molecular weight are as follows:

Structural formula:

Empirical formula: $C_7H_6Cl_2$

Molecular weight: 161.0

1.2. PHYSICAL AND CHEMICAL PROPERTIES

Benzal chloride is a colorless, oily liquid with a pungent, aromatic odor. Some of the properties of this compound are given below: (Weast, 1979, unless otherwise noted):

Melting point:	-16.4°C
Boiling point:	205.2°C
Density:	1.2557_{14}^{14} g/mℓ
Vapor pressure at 123.6°C:	60 mm Hg
Calculated water solubility at 30°C:	250 mg/ℓ (Ohnishi and Tanabe, 1971)
Conversion factor:	1 mg/m³ = 0.152 ppm

Benzal chloride is soluble in diethyl ether and ethanol and is miscible with most organic solvents. This compound is hydrolyzed to benzaldehyde under both acid and alkaline conditions (Gelfand, 1979).

1.3. PRODUCTION DATA

Benzal chloride is manufactured by chlorinating toluene with a yield of 70% and is purified by distillation. Benzal chloride is formed also by the reaction of dichlorocarbene with benzene (Gelfand, 1979).

The U.S. EPA (1977) TSCA production inventory lists three manufacturers of benzal chloride (Kodak, Stauffer Chemical Company and Monsanto Company) with a total estimated production of 2.0-10.1 million pounds; however, according to the Directory of Chemical Producers (SRI, 1984) only Stauffer Chemical Company is currently manufacturing benzal chloride. Current United States production volume for this chemical is not known. Imports of benzal chloride have not been reported since 1971 (IARC, 1982).

1.4. USE DATA

Benzal chloride is used almost exclusively in the manufacture of benzaldehyde. Benzaldehyde is made principally by direct oxidation of toluene, and only a small fraction of the total benzaldehyde produced in the United States is made by hydrolysis of benzal chloride (IARC, 1982). Benzaldehyde is used in the manufacture of perfume, flavor chemicals, pharmaceuticals and dyes.

It has also been reported that benzal chloride can be converted to cinnamic acid by heating with sodium acetate. Cinnamic acid is not manufactured in the United States (IARC, 1982).

2. ENVIRONMENTAL FATE AND TRANSPORT PROCESSES

2.1. AIR

Pertinent data regarding the environmental fate and transport of benzal chloride in air could not be located in the available literature.

2.2. WATER

Only information concerning the hydrolysis of benzal chloride was located in the available literature; however, it would appear that this process dominates the fate of benzal chloride in water.

Laughton and Robertson (1959) investigated the rate of hydrolysis of benzal chloride at 30°C. The first-order rate constant (k_1) was 0.178 min^{-1}, corresponding to a half-life of ~4 minutes.

Colina et al. (1974) investigated the hydrolysis rate of benzal chloride over a pH range from 2-10; all measurements were made at 30°C. In all cases, the rate of hydrolysis was observed to be independent of pH. The first-order rate constant measured was 0.165 min^{-1}, indicating a half-life of ~4 minutes.

Mabey and Mill (1978) took the data of Laughton and Robertson (1959) and extrapolated it to 25°C. The rate constant for benzal chloride hydrolysis was estimated to be 0.094 min^{-1} at 25°C, corresponding to a half-life of ~7 minutes.

Since >96% of the original concentration of a compound is depleted after five half-lives, it is expected that benzal chloride will not persist in the environment. Benzal chloride will quickly hydrolyze to benzaldehyde, which in turn will be readily oxidized to benzoic acid.

2.3. SOIL

Pertinent data regarding the environmental fate and transport of benzal chloride in soil were not located in the available literature; however, the compound is expected to undergo rapid hydrolysis in moist soils.

3. EXPOSURE

The presence of benzal chloride in surface waters has been reported by Hushon et al. (1980), but concentrations were not specified. Monitoring data on the level of benzal chloride in air and foods could not be located in the available literature.

4. PHARMACOKINETICS

Pertinent data regarding the pharmacokinetic profile of benzal chloride are limited. Stein and Narang (1984) administered an extract of soil from an industrial waste site to rats at oral doses of 0, 25, 75 or 150 mg soil extract/kg/day for 20 days. The soil extract was known to contain a variety of phenolic, volatile and semivolatile compounds including α, α-dichlorotoluene (benzal chloride) and other dichlorotoluenes. No benzal chloride or other dichlorotoluenes were detected by gas chromatography in blood or liver taken from the treated rats; other tissues, urine, feces or expired air were not analyzed. The detection limits for dichlorotoluenes in these tissues spiked in vitro with the soil extract were 8 ng/g for fat, 2 ng/g for liver and 0.4 ng/mL for blood.

5. EFFECTS

5.1. CARCINOGENICITY

Because three cases of lung cancer and one case of malignant maxillary lymphoma were reported in one factory (~20 workers) manufacturing benzoyl chloride, and two cases of lung cancer were reported in another factory (~20 workers) manufacturing benzoyl chloride, Fukuda et al. (1981) investigated the carcinogenicity of benzyl chloride, benzal chloride, benzotrichloride and benzoyl chloride. After the hair was clipped from the backs of 10 (3-week-old) SPF female weanling ICR mice, 10 µl of benzal chloride was applied 3 times/week for 4 weeks. From the beginning of week 5 until the termination of the experiment at 9.8 months when the mice were killed, 10 µl of benzal chloride was applied twice weekly. None of the mice died during the experiment, but 4/10 mice developed tumors. One mouse had a skin papilloma, presumably in the area treated with benzal chloride; two mice had lung adenomas; and one mouse had both a lung adenoma and skin papilloma. The first skin papilloma appeared 187 days after treatment with benzal chloride was begun. In contrast, application of 10 µl of benzotrichloride under the same conditions resulted in the death of 8/10 mice, skin carcinomas in 4/10 mice (three squamous cell carcinomas and one basal cell carcinoma) and skin papillomas in 1/10 mice. In the control group made up of 10 female ICR mice painted with 10 µl of benzene instead of benzal chloride, but otherwise following the same protocol, none of the mice died and none had tumors at the termination of the experiment.

In a second experiment with benzal chloride, the shaved backs of 19 (7-week-old) SPF ICR mice were painted twice weekly for 11.7 months with a solution of 2.3 µl of benzal chloride diluted with benzene to make 25 µl. The control group consisted of 20 mice subjected to the same proto-

col except that benzene without benzal chloride was used to paint their backs. The animals were killed at 18.7 months, 7 months after treatment was terminated. Of the mice treated with benzal chloride, 74% were either moribund or dead at the time of terminal sacrifice, whereas 10% of control mice were dead or moribund at the time of terminal sacrifice. In the group of 19 mice treated with benzal chloride, 16 (84%) had tumors: 9 had skin squamous cell carcinomas, 2 had skin fibrosarcomas, 5 had lung adenomas and 1 had a lymphoma. The first skin tumor was detected 315 days after the start of treatment with benzal chloride. In the control group of 20 mice, 2 (10%) had lung adenomas.

5.2. MUTAGENICITY

The mutagenicity of benzal chloride was studied in the rec assay using Bacillus subtilis and in the reverse mutation assay using Salmonella typhimurium and Escherichia coli (Yasuo et al., 1978). Benzal chloride was positive for reverse mutation in S. typhimurium strain TA100 and E. coli strain WP2 hcr when tested by plate incorporation at 0, 0.6 and 1.2 μmol/plate in the presence, but not in the absence, of the S-9 fraction prepared from the livers of Aroclor 1254-treated rats. The positive response was dose-related in both bacterial systems. Benzal chloride was positive in the rec assay using B. subtilis strains H17(rec^+) and M45(rec^-) at 31 and 6 μmol/disk in the spot test. The reponse in the rec assay did not require metabolic activation.

According to the benzal chloride CHIP (U.S. EPA, 1982), benzal chloride was reported by Russian scientists to be nonmutagenic to larval or adult stages of Drosophila melanogaster when they were treated orally or exposed by inhalation to benzal chloride (Filippova et al., 1967; Bartoshevich et al., 1966). In the absence of protocol details and sample size, it is not possible to determine whether this is a valid study.

5.3. TERATOGENICITY

Pertinent data regarding the teratogenicity of benzal chloride could not be located in the available literature.

5.4. OTHER REPRODUCTIVE EFFECTS

Pertinent data regarding other reproductive effects of benzal chloride could not be located in the available literature.

5.5. CHRONIC TOXICITY

Pertinent data regarding chronic toxicity of benzal chloride could not be located in the available literature.

5.6. OTHER RELEVANT INFORMATION

The acute oral LD_{50} for benzal chloride was 2460 mg/kg bw for mice and 3250 mg/kg bw for rats (Vernot et al., 1977). The inhalation LC_{50} was 210 mg/m³ (32 ppm) for mice and 400 mg/m³ (61 ppm) for rats (Mikhailova, 1964). The acute inhalation exposure to benzal chloride caused CNS excitation, muscle twitching, irritation of the eyes and respiratory mucosa, and decreased respiratory rate. Continuous exposure of rats to 100 mg/m³ of benzal chloride resulted in weight loss.

Fukuda et al. (1981) concluded that, although workers were exposed to benzyl chloride, benzal chloride, benzotrichloride and benzoyl chloride in factories producing benzoyl chloride, benzotrichloride was responsible for the increased incidence of cancer. Rittfeldt et al. (1983), however, reported that certain types of vinyl floors emit benzal choride, and that the plasticizer, butyl benzyl phthalate, is often contaminated with benzal chloride and may be a potential source of benzal chloride exposure to workers.

It was reported in an English abstract of a Russian article that rats administered an unspecified oral dose of benzal chloride and then chroni-

cally exposed to hexamethylenediamine (1 mg/m³), benzene (5 mg/m³), toluene (50 mg/m³) or tylosin (2.1 mg/m³) in the air, developed leukocytolysis, leukergy and altered hemoglobin and white blood cell levels (Izrailet and Laivina, 1980).

6. AQUATIC TOXICITY

Pertinent data regarding the toxicity of benzal chloride to aquatic species could not be located in the available literature.

7. EXISTING GUIDELINES AND STANDARDS

7.1. HUMAN

Pertinent data regarding existing guidelines and standards for benzal chloride could not be located in the available literature. The U.S. EPA (1980), however, has classified benzal choride as a toxic waste. IARC (1982) reported that the recommended maximum level of benzal chloride in the work environment in the USSR is 0.5 mg/m^3.

7.2. AQUATIC

Pertinent data regarding existing guidelines and standards for exposure of aquatic organisms to benzal chloride could not be located in the available literature.

8. RISK ASSESSMENT

IARC (1982) reported that there was insufficient evidence to classify benzal choride as a carcinogen in humans, although there appeared to be an increase in respiratory cancer in young workers exposed to benzal chloride and related chlorotoluenes in a benzoyl chloride manufacturing plant; IARC also reported that there was limited evidence indicating that benzal chloride is a carcinogen in animals. In the skin painting experiments of Fukuda et al. (1981), there was an increased incidence of skin tumors and pulmonary adenomas in benzal chloride-treated mice compared with benzene control mice. The incidence of skin tumors greatly increased when the mice were observed for an additional 4 months after skin painting with benzal chloride had ceased, indicating that tumor development caused by benzal chloride had a significant latency period. While benzal chloride was mutagenic in bacteria (Salmonella and E. coli) and caused cell killing in a strain of B. subtilis deficient in DNA repair, the lack of data from a eukaryotic system preclude judgment concerning the mutagenicity of benzal chloride in eukaryotic systems. No data regarding the teratogenicity, reproductive effects or chronic toxicity of benzal chloride were located in the available literature. Therefore, data are insufficient to derive an ADI or a q_1^* for benzal chloride.

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APPENDIX

LITERATURE SEARCHED

This profile is based on data identified by computerized literature searches of the following:

CA SEARCH (Files 308, 309, 310, 311, 320)
TOXLINE
RTECS
OHM TADS
STORET
SRC Environmental Fate Data Bases
SANSS
AQUIRE
TSCAPP

These searches were conducted in July, 1984. In addition, hand searches were made of Chemical Abstracts (Collective Indices 7 and 8th), and the following secondary sources were reviewed:

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